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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> C08F 283/02, C08L 51/08, 67/02, C08G 63/91	<b>A1</b>	<b>(11) International Publication Number:</b> WO 97/47670 <b>(43) International Publication Date:</b> 18 December 1997 (18.12.97)
<b>(21) International Application Number:</b> PCT/US97/09543 <b>(22) International Filing Date:</b> 2 June 1997 (02.06.97) <b>(30) Priority Data:</b> 08/662,701 13 June 1996 (13.06.96) US <b>(71) Applicant:</b> REGENTS OF THE UNIVERSITY OF MINNESOTA [US/US]; Morrill Hall, 100 Church Street S.E., Minneapolis, MN 55455 (US). <b>(72) Inventors:</b> BHATTACHARYA, Mrinal; 3453 Montmorency Street, Vadnais Heights, MN 55110 (US). JOHN, Jacob; 2044 Brewster, St. Paul, MN 55108 (US). VAIDYA, Utpal; 635 Prairie Center Drive #276, Eden Prairie, MN 55344 (US). <b>(74) Agent:</b> BRUESS, Steven, C.; Merchant, Gould, Smith, Edell, Welter & Schmidt, 3100 Norwest Center, 90 South Seventh Street, Minneapolis, MN 55402 (US).		<b>(81) Designated States:</b> AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> METHOD OF GRAFTING FUNCTIONAL GROUPS TO SYNTHETIC POLYMERS FOR MAKING BIODEGRADABLE PLASTICS		
<b>(57) Abstract</b> <p>The invention provides a graft copolymer made by grafting a monomer containing a functional group to a polyester macromolecule using an addition reaction or a substitution reaction. The invention further provides a biodegradable composition that is made by melt blending the graft copolymer and a natural polymer, such as starch or protein. The invention further includes a method of making the graft copolymer using an addition reaction or a substitution reaction and a method for making the biodegradable composition by melt blending the graft copolymer and a natural polymer at an elevated temperature.</p>		

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## METHOD OF GRAFTING FUNCTIONAL GROUPS TO SYNTHETIC POLYMERS FOR MAKING BIODEGRADABLE PLASTICS

### Background of the Invention

5 Synthetic polymers are increasingly replacing conventional materials like metal, wood, glass and paper because of their excellent mechanical properties, as well as chemical and weather resistance. However, the same properties, such as durability, which make synthetic polymers desirable also make synthetic polymers nonbiodegradable. As a result, a large amount of plastic waste is accumulating in  
10 landfills and causing severe pollution. The accumulation of plastic waste has led to a growing interest in the development of biodegradable plastics. Limited oil reserves have also generated a need for degradable plastics based on renewable sources like cereal grains or cellulose.

Although biopolymers are biodegradable and derive from a renewable resource,  
15 biopolymers are difficult to mold and therefore difficult to use. Additionally, products made only from biopolymers, such as starch, tend to be brittle and inflexible and thus unsuitable for many purposes.

A composition having the performance of a synthetic polymer that is completely biodegradable is desirable. However, biopolymers and synthetic polymers are typically  
20 incompatible when blended. As a result, materials prepared from a combination of biopolymers and synthetic polymers tend to generate products with inferior physical properties. Typically, the inferior physical properties of such blends are due to poor adhesion between the natural polymer and the synthetic polymer.

It is therefore desirable to develop a practical method for producing a  
25 biodegradable composition that retains both the biodegradable properties of natural polymers and the desirable mechanical properties associated with synthetic polymers.

United States Patents Nos. 5,321,064 and 5,446,028 describe a method for producing a biodegradable composition made by melt blending synthetic polymers and natural polymers. The compositions taught by these patents retain the desirable  
30 properties of synthetic polymers. However, due to the synthetic polymers used to make the composition, the compositions are only partially biodegradable.

A composition that is completely biodegradable would be preferable. Although completely biodegradable synthetic polymers such as aliphatic polyesters (e.g.,

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polycaprolactone, polylactic acid and polyhydroxy butyrate-co-valerate) are available alternatives to non-biodegradable synthetic polymers, the cost of these materials are several times that of commodity plastics. Therefore, widespread use of these biodegradable plastics is impractical.

5 A composition that combines a biodegradable polyester and a natural polymer would still be completely biodegradable and less expensive than a composition containing only aliphatic polyesters. However, polyesters are incompatible with biopolymers because they do not contain functional groups that can interact with the functional groups present on a biopolymer. Therefore, when a polyester is combined  
10 with a biopolymer, there is no chemical or physical interaction between the polymers. Consequently, the resulting blend has poor mechanical properties. Additionally, the lack of interaction between biopolymers and polyester macromolecules limits the amount of natural polymer that can be present in a blend. As a result, the quality of the blend typically decreases with the addition of natural polymer. In their thesis, Koenig and  
15 Huang (University of Connecticut, 1994) observed that the tensile properties of a blend containing starch and polycaprolactone significantly decrease when greater than 25 wt-% of starch is added to the blend.

The quality of a polyester blend can be enhanced by modifying the polyester macromolecule. One type of modification involves an interchange reaction. L.Z. Pillon  
20 et al. "Compatibilization of Polyester/Polyamide Blends via Catalytic Ester-Amide Interchange Reaction." Polymer Engineering and Science 24(17): 1300-1305 (1984). Pillon et al. teach the modification of poly(ethylene terephthalate) by ester-amide interchange reactions with p-toluenesulfonic acid as a catalyst. The interchange reaction improves mechanical properties of blends containing poly(ethylene terephthalate) and  
25 poly(amide-6,6). However, the product of this interchange reaction is not biodegradable. Additionally, the variety of blends that can be made using this technology are limited.

Adding a functional group to a polyester macromolecule is another modification that can increase the reactivity of the polyester macromolecule and therefore improve  
30 the properties of a polyester blend. However, grafting reactions are generally not successfully performed on polyester macromolecules because polyesters are easily degraded during a typical grafting reaction. Previous attempts to graft monomers to a

polyester macromolecule have been unsuccessful. T.J. Xue, "The Interaction of Vinyl Monomers and Poly(ethylene terephthalate) in the Presence of Various Initiators Produces a Physical Mixture, not a Graft Polymer", J. of Polymer Science 33:2753-2758 (1995). Xue describes the production of a physical mixture, instead of a graft polymer, when poly(ethylene terephthalate) is combined with vinyl monomers using various initiators in solution phase. Another method for introducing reactive groups to aliphatic diols involves an interfacial polycondensation reaction with bisphenols and isophthaloyl chloride in an organic two phase system. S. Nakamura, "Preparation of Polyesters With Reactive Groups in the Main Chain or Side Chain By Organic/organic Two-phase Interfacial Polycondensation", ACS Symposium (1995) Chicago, Illinois. Although the polymerization reaction taught by Nakamura is capable of introducing reactive groups to a polyester macromolecule, the location of the reactive groups is limited to side chains because the reactive group is added to a terminal carboxylic acid.

United States Patents Nos. 3,816,566 and 3,884,994 describe a method for thermal grafting of ethylenically unsaturated compounds, such as polymers of alkyl acrylate and alkyl methacrylate, onto polycaprolactone in the presence of initiators. However, the ethylenically unsaturated compounds are not biodegradable and grafting these compounds to a polyester macromolecule does not increase the reactivity of the polyester macromolecule with biodegradable natural polymers. Therefore, the resulting copolymer can not be used to make a biodegradable composition. Instead, the copolymer taught by these patents is used as a compatibilizing agent.

Because a composition containing an aliphatic polyester and a natural polymer would be fully biodegradable, there is a need for a method to modify a polyester macromolecule with functional groups that are capable of chemically or physically interacting with a natural polymer or a synthetic polymer. Additionally, a polyester that is capable of interacting with either a natural or synthetic polymer would increase the range of potential uses for polyesters, such as use as a plasticizer or as a component in alloys and blends.

### Summary of the Invention

The present invention is directed to a graft copolymer, a biodegradable composition made from the graft copolymer, methods for making the graft copolymer and biodegradable composition, and articles made from the biodegradable composition.

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A first aspect of the invention is directed to a graft copolymer made by grafting a monomer containing a functional group to a polyester macromolecule under conditions where the polyester macromolecule does not substantially degrade. As a result of the grafting reaction, the polyester graft copolymer has at least one functional group with which it can interact with another synthetic or natural polymer. The grafting reaction can be an addition reaction, preferably a free radical initiated grafting technique, or a substitution reaction. Either reaction is preferably performed by melt blending, although either reaction can also be accomplished in solution.

A second aspect of the invention is directed to a biodegradable composition.

The biodegradable composition is made by melt blending, at an elevated temperature, the polyester graft copolymer described above and a natural polymer, such as starch or protein. The functional groups on the polyester graft copolymer are capable of interacting chemically or physically with a functional group, such as a hydroxyl or an amine, present on the natural polymer.

The biodegradable composition has a continuous phase and a dispersed phase. One phase contains a biodegradable material, such as a natural polymer. The other phase contains a biodegradable polyester graft copolymer. At least a few molecules of the graft copolymer and at least a few molecules of the natural polymer chemically or physically interact at the interface between the dispersed phase and the continuous phase.

A third aspect of the invention is directed to methods for making the graft copolymer and the biodegradable composition. The graft copolymer is formed by grafting a monomer to a polyester macromolecule under conditions which minimize degradation of the polymer. Preferably, the grafting reaction is an addition reaction, such as a free radical initiated grafting technique, or a substitution reaction. Either reaction can be accomplished by melt blending the polyester macromolecule and monomer under an inert atmosphere. The biodegradable composition described above is then formed by melt blending the graft copolymer and a natural polymer.

A fourth aspect of the invention is directed to a biodegradable article of manufacture produced by injection molding, extruding, thermofolding, die cutting, film blowing, sheeting or compression molding the biodegradable composition taught by the present invention.

### **Detailed Description of the Invention**

In general, a graft copolymer is recognized in the art and defined according to the present invention to be a macromolecule made up of two components: a backbone component and a graft component where the graft component is attached to the backbone component at an active site other than at the end of the backbone component. The active site can be formed by a reaction where a free radical initiator abstracts a hydrogen atom from the backbone component thereby forming an active site on the backbone component. Alternatively, a reactive group that is already present on the backbone component, such as a carboxylic acid residue, can be used as an active site. Subsequent exposure of the active site on the backbone component to a graft component results in bond formation between the two components.

The graft copolymer of the present invention can be formed by an addition reaction, such as a free radical initiated grafting technique, or a substitution reaction. In either case, the backbone component is a polyester macromolecule and the graft component is a monomer containing a functional group.

Because polyester macromolecules tend to degrade under typical grafting conditions, the present invention is directed to a method of making a graft copolymer having a polyester backbone component wherein the polyester macromolecule is not substantially degraded during the grafting reaction. As a result, the molecular weight of the graft copolymer (the product) is similar to the molecular weight of the polyester macromolecule (the starting material).

If a polyester macromolecule is subject to excessive degradation during grafting, mechanical properties of the final product may be adversely affected. For example, degradation of the polyester macromolecule can result in a loss of tensile strength and elongation. Additionally, increased crosslinking between the degraded polyester molecules can cause the final product to be brittle and difficult to mold. Therefore, it is important to maintain the amount of degradation of the polyester macromolecule within an acceptable range.

Because the conditions under which a polyester macromolecule degrades vary among different polyester macromolecules, optimal reaction conditions will vary depending on which polyester macromolecule is used. Additionally, the acceptable

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amount of degradation will vary depending upon the intended use and required mechanical properties of the final product. For example, if the graft copolymer is ultimately going to be combined with a natural polymer to form a biodegradable composition that will be molded or drawn out in a sheet, the polyester backbone component should be sufficiently intact such that the biodegradable material retains sufficient tensile strength and elongation and is not brittle. However, if the polyester macromolecule does degrade during the grafting reaction and the physical properties of the blend are not important, the blend can still be used. Alternatively, the properties of the blend can be improved by adding a higher percentage of graft copolymer to the blend.

10 The grafting reaction can be performed as either an addition reaction, such as a free radical initiated grafting reaction, or a substitution reaction. A suitable free radical for the free radical initiated grafting reaction of the present invention is capable of activating the polyester macromolecule by abstracting a hydrogen atom. The free radical initiator can be generated by thermal or photochemical decomposition of an organic peroxide, 15 inorganic peroxide, peroxosalt, transition metal salt, hydroperoxide, azo compound, and the like. The half life of the free radical should be long enough so that the free radical is available throughout the grafting reaction, but not so long that the free radical persists after the reaction is completed. Lingering free radicals might degrade the graft copolymer. Therefore, a suitable free radical initiator can be selected by determining the temperature 20 at which the reaction will be run and then finding a free radical that has a half life from about 0.1 hours to 1.0 hour under the reaction conditions. A preferred free radical initiator is an organic peroxide with a half life from about 0.1 hours to about 2.0 hours when present in a temperature range from about 80°C to about 200°C. Examples of suitable organic peroxide initiators include di-t-butyl peroxide, dicumyl peroxide, dibenzoyl 25 peroxide, azo-bis-isobutyronitrile, t-butylhydroperoxide, lauryl peroxide, di-isopropylperoxy-di-carbonate, and the like.

During the grafting reaction, the initiator should be present in a concentration that is effective to produce a graft copolymer with the desired degree of functionality. Although the concentration of the initiator in the grafting reaction mix (which includes 30 polyester macromolecule, initiator and monomer) can vary widely, a preferred concentration range for the initiator is from about 0.01 wt-% to about 5.0 wt-% of the



reaction mix. More preferably, the concentration of the initiator is from about 0.1 wt-% to about 1.0 wt-%.

Alternatively, the grafting reaction can be performed as a substitution reaction. In a substitution reaction, reactive groups that are present on the side chain of a polyester macromolecule are replaced by another group. For example, acyl compounds or carboxylic acids and their derivatives might undergo a reaction in which a hydroxyl, halide, ester, amine, or ether is replaced by a functional group attached to a monomer.

Both the free radical initiated grafting reaction and the substitution grafting reaction are preferably accomplished by melt blending in an intensive mixer or a single or twin screw extruder. Melt blending is the preferred method because it is relatively fast. Additionally, flammable or expensive solutions are unnecessary. As a result, melt blending results in a product that is less expensive, safer to make, has a high yield and does not require further purification.

Although melt blending can be used to form a physical mixture, in the present invention melt blending uses a combination of increased temperature and shear stress to liquefy the reactants so that their functional groups can more easily interact. In a preferred embodiment, the extruder has multiple zones in which the temperature can be individually controlled. Therefore, the temperature of the reaction is easily controlled and can be varied according to the needs of a particular reaction. Additionally, the shear stress, due to pressure and/or friction generated during melt blending, reduces the temperature required to liquefy the polyester macromolecule. Therefore, high temperatures that can cause degradation of the polyester macromolecule are avoided.

The temperature range at which the reaction is run should be high enough that a sufficient amount of grafting will occur, but not so high that excessive degradation of the polyester macromolecule occurs. If the grafting reaction is performed at temperature at which the unreacted monomer will undergo sublimation or vaporization, unreacted monomers can be eliminated by use of a vacuum. Because the sublimation and/or vaporization temperature varies depending on which monomer is used, the sublimation and/or vaporization temperature of the monomer can be one factor that affects the temperature at which the grafting reaction is run.

The melting temperature of the polyester macromolecule is another factor that affects the optimal temperature at which the grafting reaction is performed. The grafting

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reaction is preferably carried out at a temperature that is near or above the melting temperature of the polyester macromolecule. Therefore, for many polyester macromolecules, the grafting reaction can be performed in a temperature range from about 80°C to about 300°C. A temperature for a specific reaction is selected such that the monomers and the polyester macromolecules have the desirable properties discussed above. The melting point of a polyester macromolecule and the sublimation and/or vaporization temperature of a monomer are easily determined by one with skill in the art. For example, when the polyester macromolecule is polycaprolactone, the grafting reaction is preferably performed in a temperature range from about 80°C to about 200°C. On the other hand, when the polyester macromolecule is poly(ethylene terephthalate), the grafting reaction is preferably performed in a temperature range from about 200°C to about 300°C.

The length of time that the grafting reaction is allowed to run will affect the amount of degradation of the polyester macromolecule. Additionally, the duration of the grafting reaction will influence the amount of grafting that occurs. The reaction is therefore run for a duration that is sufficient to graft an effective amount of functional groups to the polyester macromolecule, but not so long that the polyester macromolecule is excessively degraded. Typically the melt blending reaction is allowed to run from about 30 seconds to about 15 minutes. Preferably, the reaction is allowed to run from about 2 minutes to about 10 minutes. More preferably, the melt blending reaction is run from about 7 minutes to about 10 minutes.

If a free radical initiated grafting technique is performed by melt blending, the reaction is preferably performed under a non-oxidizing atmosphere because oxygen can quench the free radical. A suitable non-oxidizing atmosphere contains an inert gas such as nitrogen, argon, helium, and the like. If a substitution reaction is performed by melt blending, it is preferred that the reaction occur under a gas stream, such as nitrogen, to remove small by-products such as water vapor or hydrochloric gas that might be formed during the substitution reaction. It is also preferred that the grafting reaction be performed in bulk to avoid homopolymerization of the monomer.

In an alternative embodiment, the grafting reaction can be performed in solution. If the goal of the grafting reaction is to add reactive groups to the polyester macromolecule to enhance its reactivity with a natural polymer, it is preferred that the reaction be performed using a non-polar solvent. The presence of a polar molecule could hydrolyze

functional groups present on the monomer, such as anhydrides, that are capable of interacting with the functional groups on a natural polymer. Additionally, a polar solvent could degrade the polyester macromolecule. Suitable non-polar solvents include benzene, xylene, toluene, and the like. It is also preferred that the non-polar solvent is purged of water or polar molecules. Preferably the solution reaction is performed using a solvent that is compatible with both the monomer and the polyester macromolecule. However, if such a solution is not available, the reaction can be performed using a two phase system.

The solution reaction should be performed at a temperature that is high enough to increase the rate of reaction, but not so high that the polyester macromolecule is degraded. Preferably, the reaction is performed at a temperature from about 25°C to about 200°C, more preferably from about 40°C to about 150°C. The solution reaction is run for an amount of time that is effective to graft a sufficient number of reactive groups to the polyester macromolecule. The solution reaction can be run from about 30 minutes to two days. More preferably, the reaction is run from about 30 minutes to 4 hours.

If the substitution reaction is performed in solution, it is preferred that the solution contain a neutralizing agent such as pyridine that will neutralize hydrochloric acid that might be formed during the reaction.

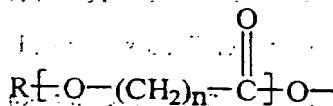
According to the present invention, the functional groups on the monomers provide a reactive site for interaction with various natural and synthetic polymers. If the graft copolymer is to be combined with a natural polymer to form a biodegradable composition, the graft copolymer should preferably have a graft content such that the polyester macromolecule will effectively interact chemically or physically with another polymer to form a biodegradable composition with desirable mechanical properties. However, an excessive amount of functional groups can result in excessive crosslinking which can make the blend difficult to process. Typically, the graft copolymer has a graft content from about 0.1 wt% to about 20 wt%. More preferably, the graft content is from about 0.3 wt-% to about 10 wt-%. The preferred graft content will also vary depending on the natural polymer with which the graft copolymer is to be combined. For example, if the graft copolymer is going to be combined with starch to make a biodegradable composition, it is preferred that the graft content be from about 0.2 wt-% to about 5 wt-%. If the graft copolymer is going to be combined with a protein, it is preferred that the graft content be from about 0.2 wt-% to about 2 wt-%.

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Although the grafting reaction can be used to attach a monomer to both aliphatic or aromatic polyester macromolecules, if the polyester macromolecule is going to be used to make a biodegradable blend, it is preferably an aliphatic polyester macromolecule with a molecular weight from about 5,000 kDa to about 150,000 kDa. An aliphatic polyester macromolecule is used because aliphatic polyester macromolecules have desirable mechanical properties and, unlike many other synthetic molecules, are completely biodegradable. Polyester macromolecules are biodegradable because enzymes, such as depolymerase, cellulase, esterase, alcaligenes eutrophus, alcaligenes faecalis, and the like, that are found in the digestive system of microorganisms are capable of digesting ester linkages and can therefore break down the polyester macromolecule and use the components as an energy source.

If the graft copolymer is to be combined with a natural polymer to form a biodegradable composition, then the aliphatic polyester preferably has a melting point of less than 200°C, such that the natural polymer is not burned or degraded during the melt blending process described below. If the graft copolymer is going to be combined with another synthetic polymer, such as nylon, and biodegradability is not a concern, either an aliphatic or aromatic polyester macromolecule can be used as the backbone component of the graft copolymer. Additionally, the melting point of the polyester macromolecule can be at a higher temperature if the graft copolymer is not going to be combined with a natural polymer.

The polyesters of particular interest employed in this invention can be represented by the following repeating units:



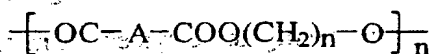
wherein R is an hydrogen atom or an alkyl group containing from about one to about six carbon atoms and n is an integer from three to eight.

Examples of suitable polyester macromolecules include polycaprolactone, polylactic acid, esters of polyglycols, poly hydroxy butyrate-co-valerate and the like. Suitable esters of polyglycols include ethylene glycol, propylene glycol, diethylene glycol, butane diols, polyglycolic acid, and the like. Other suitable polyester macromolecules include those derived from a polycondensation reaction with an aliphatic dicarboxylic acid

such as glutaric acid, adipic acid, succinic acid, and other higher acids with the general formula shown below:

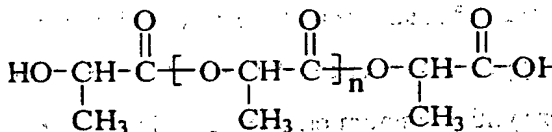


5 Aromatic polyesters that are suitable for use in the grafting reaction include aromatic esters derived from phthalic, isophthalic and terephthalic compounds, alkyl substituted phenols, and the like. The aromatic esters that can be used are represented by the general formula:



10 where A is an aromatic ring and n is an integer.

The polylactides employed according to the method of the present invention can be represented by the following:



15 where n is an integer.

According to the present invention, a monomer containing a functional group is grafted onto the polyester macromolecule to increase the reactivity of the polyester macromolecule. The monomer can be grafted to the backbone of the polyester macromolecule or to a side chain on the polyester macromolecule. Preferably, the monomer contains a functional group that is capable of reacting, by the formation of covalent bonds, Van Der Waals forces, hydrogen bonds, ionic bonds, and the like, with a functional group present on another polymer, either synthetic or natural. If the graft copolymer is going to be combined with a natural polymer to form a biodegradable composition, the monomer preferably contains a functional group that is capable of reacting with a functional group on a natural polymer, such as a hydroxyl or amine. The functional group present on the monomer is preferably selected from the group consisting of primary, secondary, and tertiary amines, anhydrides such as an anhydride of a dicarboxylic acid, oxazoline, epoxy, hydroxy, isocyanate, carboxylic acid, acid chloride, aldehydes, ketones, acyl halides, alkyl halides, nitrile, nitro, thiols, esters,

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ethers, alkoxy, urethanes, urea, carbodiimide, amides, and the like. More preferably, the functional group is selected from the group consisting of primary, secondary, and tertiary amines, anhydrides such as the anhydride of a dicarboxylic acid, oxazoline, epoxy, hydroxy, isocyanate, carboxylic acid, acid chloride, aldehydes, ketones, acyl halides, alkyl halides, nitrile, thiol, esters, urethanes, urea, carbodiimide, and amides.

Examples of monomers that are suitable for use in the grafting reaction include acid anhydrides, cyclic carboxylic acids, styrenes, substituted pyridines, isocyanates, oxazolines, dicarboxylic acids, functional derivatives of carboxylic acids, and the like. In particular, suitable monomers include maleic anhydride, citraconic anhydride, 2,3-dimethyl maleic anhydride, n-octodacyl succinic anhydride, maleic acid, crotonic acid, and the like.

The properties of the graft copolymer depend upon the number of reactive groups attached to the polyester macromolecule and reaction conditions such as temperature, initiator concentration, monomer concentration and also the mode of addition of the monomer to the reaction mixture. Because the graft copolymer can have various properties, the graft copolymer can be used in diverse applications. Naturally occurring polymers such as wheat gluten and starch can be converted to useful products by combining them with the graft copolymer of this invention to make a biodegradable composition. A biodegradable composition made of about 5 wt-% to about 25 wt-% of the graft copolymer is completely biodegradable but also has desired mechanical properties such as tensile strength and elongation. Other applications for the graft copolymer include its use as a plasticizers during processing reactions or as a compatibilizing agent. Once formed, the graft copolymer can be pelletized for future use or directly processed to the desired end product.

According to the present invention, the polyester graft copolymer is melt blended with a natural polymer to make a biodegradable composition having two phases, a continuous phase and a dispersed phase. The continuous phase is the major component and the dispersed phase is the minor component. For example, when the natural polymer is the major component it is considered to be in a continuous phase, whereas the synthetic polymer would be the dispersed phase. During melt blending, the graft copolymer and natural polymer chemically or physically bond at the interface between the continuous phase and the dispersed phase thereby forming a plurality of

interpolymers which effectively provide a strong interaction between the continuous phase and the dispersed phase.

In the biodegradable composition of the invention, the dispersed phase comprises a plurality of particulate microdomains having a diameter from about 0.01  
5 microns to about 100 microns. From about 0.1% to about 99%, more preferably, from about 0.1% to about 50% of the functional groups of the graft copolymer of the composition are chemically or physically bonded to the natural polymer.

The mechanical properties of the blend depend on the shape and size of the dispersed phase. Other factors contributing to the mechanical strength of the blend  
10 include the adhesion between the two phases. Because the addition of functional groups to the polyester macromolecule improves adhesion between the continuous phase and the dispersed phase, the dispersed phase has a more uniform and smaller microdomain size. Therefore, improved adhesion results in improved mechanical strength of the blend. Poor adhesion between the two phases can lead to subsequent failure of the  
15 product blend, such as tearing.

As discussed above, in connection with the formation of the graft copolymer, melt blending is a process by which the functional groups of the reactants, in this case, the graft  
20 copolymer and another polymer, are allowed to react. Instead of using a solution to enable the functional groups to react, melt blending places the reactants in a closed environment where they are reacted at an elevated temperature. The shear stress from melt blending enables the macromolecules to behave as if in a liquid state such that the reactive groups of the polymers to come into close proximity and can physically or chemically interact. Additionally, melt blending leads to a more uniform dispersion of the graft copolymer within the composition when compared to traditional blending techniques.

25 Although melt blending can cause some degradation of the polymers, functional groups on the polymers can still react to form a mixture of graft, block and crosslinked structures. When the graft copolymer is made using an aliphatic polyester macromolecule for the backbone component, a composition formed by combining the graft copolymer with a natural polymer is not only completely biodegradable, it also has excellent  
30 mechanical properties due to the enhanced interaction between the graft copolymers and the natural copolymers.

Melt blending can be performed in any reaction type vessel such as an intensive mixer, melt mixer, single screw extruder, twin screw extruder, or an injection molding machine. The residence time of the material in the extruder during melt blending should be long enough so that the functional groups have time to react, but not so long that excessive crosslinking or degradation occurs. If the resulting composition contains too much crosslinking, it will be difficult to process. Residence times of about 10 seconds to 20 minutes are preferred. More preferably, residence times are from about 45 seconds to about 10 minutes. The composition can then be directly processed to the desired end product or can be pelletized for future use.

If a biodegradable composition is being made, the temperature of the melt blending reaction should be high enough so that the reactant polymers are plasticized and their functional groups can interact, but not so high that the natural polymer burns or degrades. Preferably, the graft copolymer and natural polymer are mixed together at a temperature from about 25°C to about 200°C. More preferably, the polymers are combined at a temperature from about 90°C to about 170°C.

By the process of the invention, a biodegradable composition containing up to 99 wt-% of a natural polymer can be made. The biodegradable composition is typically in solid form at ambient temperatures after melt blending is complete, and can be either rigid or flexible depending on the nature of the natural polymers, the amount of functional groups present, and the ratio of natural polymer to graft copolymers.

A variety of naturally occurring biodegradable polymers can be used to make the biodegradable composition of the invention. The natural polymers present in the composition enhance the biodegradability of the composition because the natural polymers act as a nutrient source for living microorganisms such as bacteria and fungi. As a result, the composition can be biodegraded when it is in an environment where microbes are present. Because ester linkages of the polyester macromolecule can also be digested by microorganisms, the entire composition is completely biodegradable.

Suitable natural polymers can be derived from corn, wheat, potato, sorghums, tapioca, rice, arrow root, sago, soybean, pea, sunflower, peanut, gelatin, milk, eggs, and the like. Such natural polymer materials include carbohydrates such as starch and cellulose, lignin, proteins, nucleic acids, amino acids, and lipids, which are all



biodegradable. These natural polymers can be used either separately or in various mixtures in formulating the biodegradable composition of the invention.

One preferred class of natural polymer is carbohydrates. Within the general class of carbohydrates are saccharides or sugars, a group of organic compounds related by molecular structure. Each sugar consists of a chain of two to seven carbon atoms (usually 5 or 6). One of the carbons carries aldehydic or ketonic oxygen which may be combined in acetal or ketal forms and the remaining carbon atoms usually bear hydrogen atoms and hydroxyl groups. The carbohydrate sugars useful in the invention include monosaccharides such as glucose, fructose, saccharose, and the like; disaccharides such as lactose, maltose and sucrose; oligosaccharides; and polysaccharides like gums, starch, cellulose, etc. As used in the present specification, the term "oligosaccharide" denotes a sugar polymer of from 3 to 15 units, and a higher sugar polymer having more than 10 units is designated as a "polysaccharide". The carbohydrate component employed in the present invention can also comprise various derivatives of the above sugars, preferably ester or ether derivatives of the sugars.

A preferred carbohydrate employed in the present invention is a polysaccharide. Polysaccharides are widely distributed in the plant and animal worlds, serving as a food reserve substance and structural material. Suitable polysaccharides include starch and cellulose, which consist of D-glucopyranosyl units linked by alpha and beta-1,4 bonds, respectively.

Starch is a particularly preferred polysaccharide for use in the invention. Starches are polysaccharide compounds which on hydrolysis produce sugars. Starch can include a mixture of linear (or amylose) and branched (or amylopectin) components. Amylose has a molecular weight of several hundred thousand, while amylopectin has a molecular weight in the order of several million. Starches containing 0 to 100% amylose or 0 to 100% amylopectin can be employed in the invention. Any form of starch can be used in the present invention, including gelatinized starches, ungelatinized starches, substituted starches, chemically modified starches, crosslinked starches and unmodified starches. A variety of functional groups discussed in more detail below may be attached to the above starches. High amylose starches such as "Amalean-1" supplied by American Maize Products Company, and industrial corn starch such as

"Silver Medal Pearl-1100 (SMP-1100) supplied by Cargill Inc. are suitable starches for use in the invention.

Proteins are another natural polymer that is suitable for use with the present invention. Proteins are nitrogen organic compounds of high molecular weight from about 3000 to many millions. Proteins are made up of complex combinations of simple amino acids, and they occur in all animal and vegetable matter. The constituent amino acids of the protein molecule are linked together with a peptide bond and the linkage forms the backbone of the molecule. Suitable proteins that may be utilized in the present invention include egg proteins, milk proteins, animal proteins, vegetable proteins and cereal proteins. Examples of proteins which can be utilized in the present invention include isolated soy proteins such as "Supro 90", "Supro HD90", and "Supro 500E", which contain 90% protein and are supplied by Protein Technologies International. Wheat gluten is another source of protein that can be used.

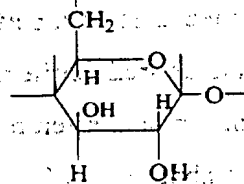
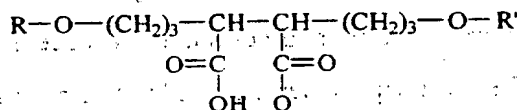
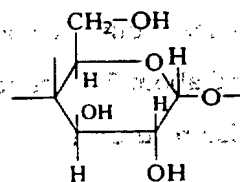
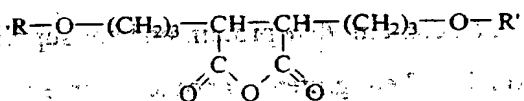
Natural materials which contain both protein and starch can also be used in the present invention. Wheat flour, such as "ICPS RED" and "ICWRS", which contain about 20% protein and about 70% starch, is such a suitable material.

Lipids may also be used as a natural polymer in the present invention. Lipids or fats are natural combinations of glycerin with fatty acids, known as triglycerides. Lipids are derived from animal or vegetable sources, the latter source being chiefly the seeds or nuts of plants. Suitable lipids that may be used in the present invention include fats derived from vegetable sources such as oil seeds.

The graft copolymer is mixed with a natural polymer in a quantity that is sufficient to enhance the mechanical properties in the resulting composition. The range of compatibility and desired tensile properties can be obtained over a wide range of weight percent of the materials. Preferably, the natural polymer is present in an amount from about 5 wt-% to about 99 wt-%, more preferably about 10 wt-% to about 80 wt-%. The properties of the composition vary depending on what polyester macromolecule is used and the quantity of functional groups present on the graft copolymer. More functional groups result in increased cross-linking which will increase the tensile strength of the molecule and decrease the flexibility or elongation of the blend. The tensile strength of the biodegradable composition will vary depending on the polyester macromolecule used and the intended use of the biodegradable composition. The tensile strength of the

biodegradable composition is close to or better than the tensile strength of a composition containing only polyester macromolecules. However, the biodegradable composition typically has a tensile strength between about 5 MPa to about 50 MPa, more preferably, from about 10 MPa to about 40 MPa.

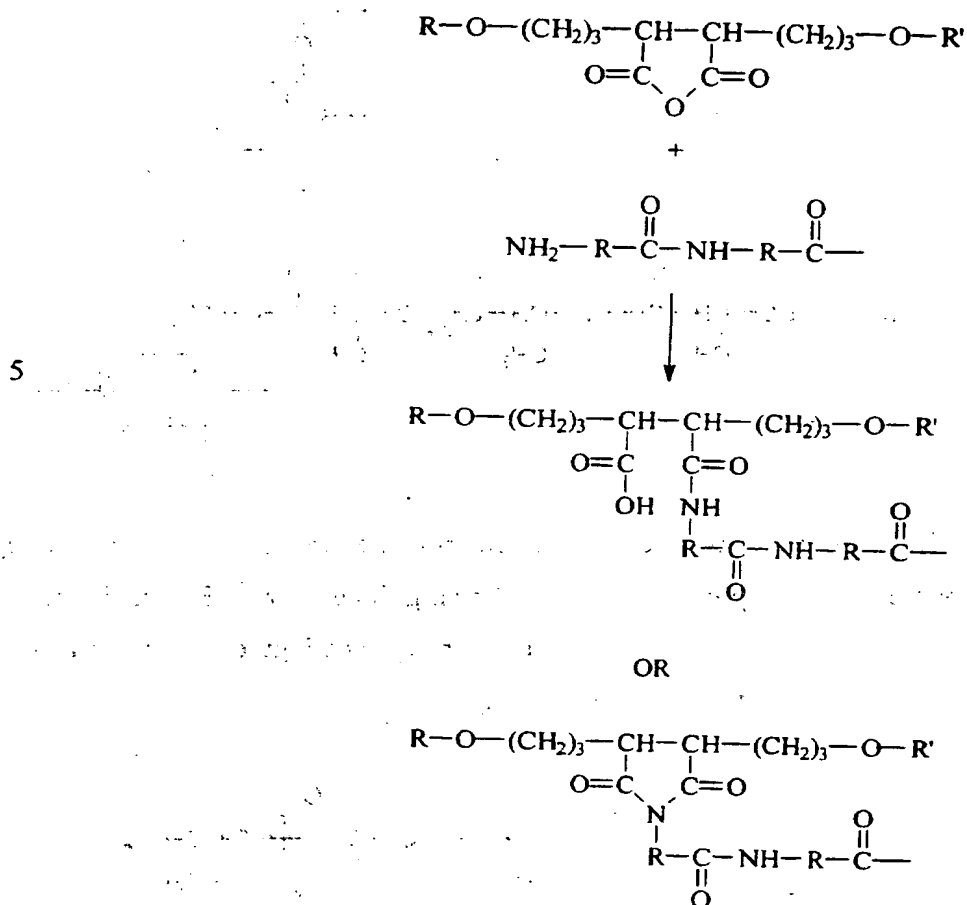
5 The possible chemical reactions between a graft copolymer with an anhydride functional group and a carbohydrate, protein or amino acid are represented below in equations 1 and 2. The anhydride and free carboxylic groups of the graft copolymer can react with the hydroxyl of the carbohydrate to form ester linkages, and with the amine groups of proteins or amino acids to form amide or imide linkages. The reaction of an  
10 anhydride group on the backbone of a graft polyester with a hydroxy group of a carbohydrate according to the present invention is shown in Equation 1 below.



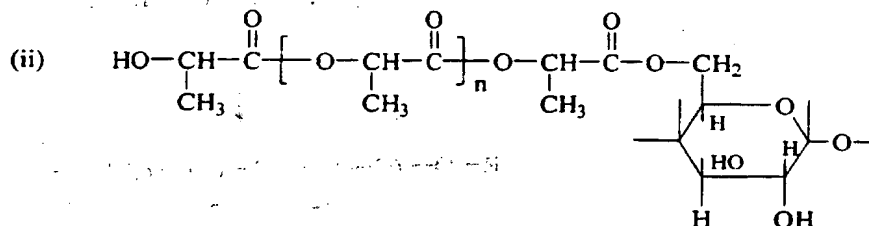
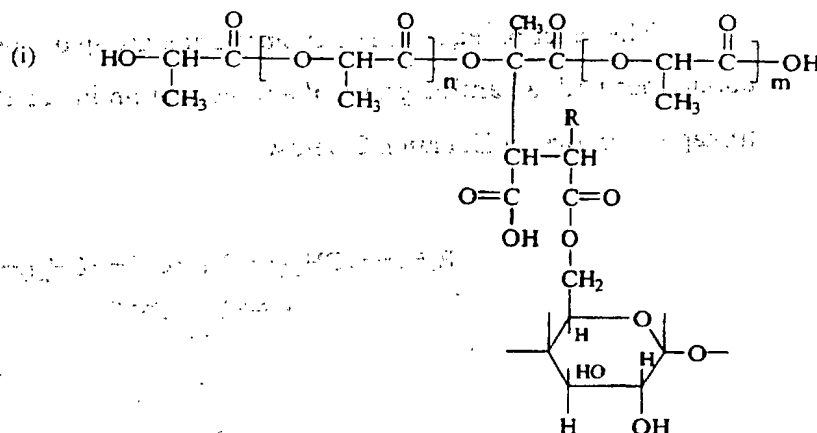
15 Although Equation 1 shows the reaction at one hydroxyl site on the carbohydrate molecule, the reaction can occur at any hydroxyl site on the carbohydrate molecule. The moieties R and R' in Equation 1 can be a polyester chain, hydrogen, halogen, alkyl, phenyl, alkoxy or various other groups.

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The reaction equation of an anhydride group on the backbone of a graft copolymer with an amine group of a protein or amino acid to form an amide or imide linkage is shown in Equation 2 below.

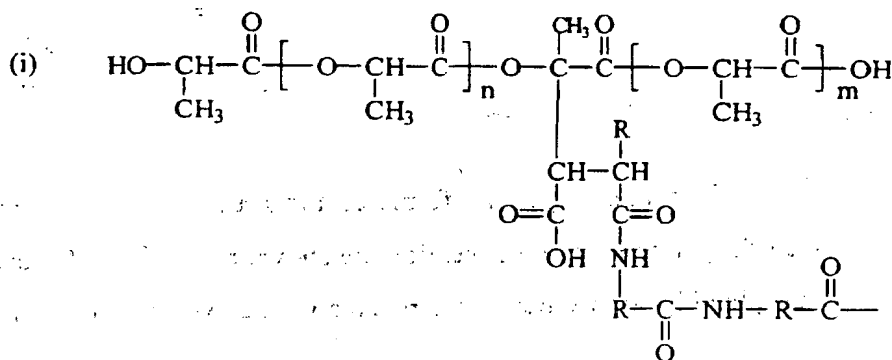


10            Examples of general formulas and structures of a biodegradable composition according to the present invention are shown below. The following two structures show a polylactide copolymer that is reacted with a hydroxyl of a carbohydrate.



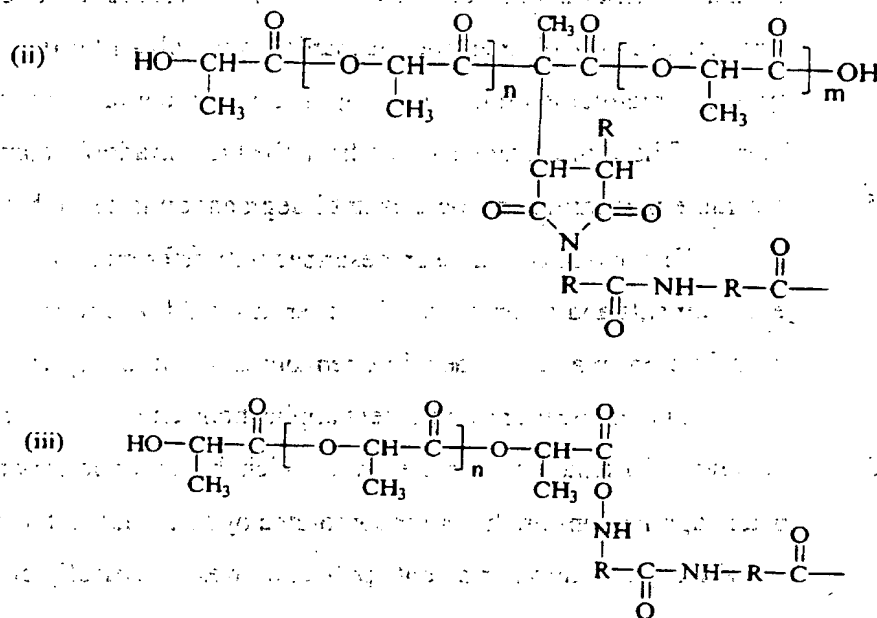
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When a protein is used as the natural polymer, the structure of the biodegradable composition can be represented by the following three figures. Figure (i) shows an amide linkage, Figure (ii) shows an imide linkage and Figure (iii) shows a polylactide with a protein grafted to a terminal hydroxyl.



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R can be hydrogen, halogen, alkyl, phenyl, alkoxy or various other groups.

Various additives can be added to the composition of the invention before or during processing. Examples of such additives include adjuvants, fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, pigments, extenders, etc. The additives can be added to the composition singly or in various mixtures.

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The biodegradable composition can be further processed by a single screw extruder, twin screw extruder, injection molding, compression molding, blow molding, thermoforming, die cutting, film blowing, sheeting, and the like, to produce various biodegradable articles.

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For example, compression molding of the composition is preferably at a pressure from about 2.0 tons to about 17.5 tons. More preferably, compression molding is at a pressure from about 5.0 tons to about 15.0 tons. In a process for producing a biodegradable article by casting or blow molding the biodegradable composition of the invention, the process takes place at a temperature of about 25°C to 250°C.

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Various articles or products which can be formed by the above processing techniques include films, foams, sheets, pipes, rods, bags, boxes, meat trays, egg cartons, hard or foam cups and plates, bowls, eating utensils, loose fill packaging materials, insulation and soundproofing materials, bottles, wrapping materials, disposable pens and razors, packaging cartons, containers and the like. Because the

natural polymer is less soluble in water after melt blending, due to the bond formation with the graft copolymer, the mechanical strength and integrity of the composition is typically maintained until the composition is in contact with the soil, buried or partially buried. Therefore, articles made from the biodegradable composition retain their desirable mechanical properties until degradation is desirable.

The invention has been described with reference to various specific and preferred embodiments and techniques. However, it should be understood that many variations and modifications may be made while remaining within the spirit and scope of the invention.

The publications and patent applications cited in this specification are indicative of the level of ordinary skill in the art to which this inventions pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated by reference.

### EXAMPLES

The graft copolymers in the following examples were analyzed for maleic anhydride using a back titration method with ethanolic KOH using 1% thymol blue in dimethyl formamide (DMF) as an indicator. The samples were extracted with xylene and reprecipitated in methanol to remove any unreacted maleic anhydride present, if any (most unreacted maleic anhydride was removed through sublimation). When the estimation was carried out without extracting the grafted product, traces of unreacted maleic anhydride was detected using a calculation based on the total amount of monomer added to the reaction. However, unreacted maleic anhydride does not adversely affect the properties of the end product.

FTIR spectra of the graft copolymer after extraction with xylene gave two absorption bands at  $1782\text{ cm}^{-1}$  and  $1861\text{ cm}^{-1}$ . These bands are assigned to the grafted anhydride because cyclic anhydrides, such as maleic anhydride, exhibit an intensive absorption band near  $1780\text{ cm}^{-1}$  and a weak band near  $1850\text{ cm}^{-1}$  due to symmetric and asymmetric stretching of  $\text{C}=\text{O}$  respectively. This confirms that anhydride groups were grafted to the polyester macromolecule because the FTIR spectra of a physical blend of maleic anhydride with the polyester macromolecule does not show any absorption around this region after extraction with xylene.

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After the anhydride content of the graft copolymer was determined, the samples were compression molded and the tensile properties of the molded samples was examined.

The materials used in the listed examples include:

Poly lactic acid resin from Cargill Incorporated, USA; Polycaprolactone (PCL 787 and PCL 767E) from Union Carbide Chemicals and Plastic Co., Inc., USA; Dicumyl peroxide, Maleic Anhydride and Trimellitic anhydride chloride from Aldrich Chemical Company, USA; and wheat gluten from Manildra Milling Corp., USA.

Examples 1-8 were performed using a C.W. Brabender Plasticorder batch mixer (C.W. Brabender Instruments Inc. N.J.). The mixer was equipped with an electrically heated mixing device with a capacity of 50 ml. The roller blades were connected through a variable speed motor such that the mixing speed could be controlled through the motor. In all examples, a flow of nitrogen gas was maintained over the mixing chamber using a gas inlet device.

#### Example-1

A polycaprolactone (PCL 787) was used as the polyester macromolecule in this example. The PCL was dried in a vacuum oven at 50°C for 24 hours to remove any volatile materials adhering to it. After the mixing chamber was purged with nitrogen, 40g of the polyester macromolecule was added to the mixer at 80°C with a speed of 60 rpm. A mixture of 3.2g of maleic anhydride and 0.4g of dicumyl peroxide were then added to the mixture. The reaction was continued for 7 to 10 minutes under a blanket of nitrogen. The reaction mixture was immediately removed from the reaction chamber after the 7 to 10 minute mixing period. The grafted anhydride content was 0.70% by weight.

#### Example-2

The reaction in Example 1 was carried out using PCL 767E as the polyester macromolecule. The grafted maleic-anhydride content was 0.80% by weight.

#### Example-3

40 g of a polylactide resin was placed into the reaction chamber at 170°C. A mixture of 3.2g of maleic anhydride and 0.4g of dicumyl peroxide were added to the



reaction chamber. The reaction mixture was mixed for 10 minutes under a nitrogen atmosphere. The anhydride content of the graft copolymer was 0.86% by weight.

#### Example-4

5 40g of PCL 787 was placed in the reaction vessel at 100°C with a screw speed of 60 rpm. A flow of nitrogen gas was maintained over the reaction vessel to remove gas formed during the substitution reaction. 3.2g of trimellitic anhydride chloride (TMAC) was added to the reaction vessel and mixed for 10 minutes.

#### Example-5

10 15g of the graft copolymer made in Example 1, was mixed with 35g of wheat gluten in an intensive mixer for 10 minutes at 100°C under nitrogen atmosphere with a speed of 60 rpm. After 10 minutes, the mixture was immediately removed from the intensive mixer.

#### Example-6

15 12.5g of PCL 787 and 2.5g of the graft copolymer containing polycaprolactone and maleic anhydride (PCL-g-MAH) made in Example 1, were mixed with 35g of wheat gluten for 10 minutes under conditions similar to that of Example 5.

#### Example-7

20 15g of the graft copolymer from Example 1 was mixed with 35g of starch in an intensive mixer for 10 minutes at 130°C under conditions similar to those in Example 5.

#### Example-8

25 35 g of Gluten and 15 g of unmodified PCL (787) was mixed in an intensive mixer for 10 min. at 110°C under conditions similar to example 5.

The samples obtained from Examples 5-7 were compression molded using Power-Twin compression molding equipment of 17.5 ton capacity to get ASTM specified tensile  
30 bars for the tensile test. The tensile strength of the samples was obtained from MTS tensile testing machine with a cross head speed of 3 mm/min. Table 1 below summarizes

the tensile strength and elongation values of unmodified, modified and the blend of modified polymer with wheat gluten and starch.

The tensile strength test of the blended composition of gluten shows enhanced tensile properties when compared to physical blends of same composition (Table 1). This again confirms the chemical bond formation during the blending process.

**Table I.**

**Properties of the grafted PCL and their blends with gluten/starch.**

10

<b>Expt#</b>	<b>Material</b>	<b>Tensile Force(MPa)</b>	<b>% Elongation</b>
Control	PCL 787	22.0	>850.00
Control	PCL 767	26.0	>1000.0
Control	PLA	50.0	14.5
1	PCL787-g-MAH	25.6	1070.0
2	PCL767-g-MAH	19.5	6.6700
3	PLA-g-MAH	89.8	11.400
4	PCL787-g-MAH	not recorded	not recorded
5	PCL787-g-MAH+Gluten	23.0	7.8000
6	PCL787-g-MAH(5%)+ PCL787(25%)+Gluten	22.0	7.7200
7	PCL787-g-MAH+Starch	21.5	9.0000
8	PCL787+Gluten	5.6	2.5000

The gluten/starch content of the samples in Table I is 70% by weight at a temperature of 110°C and a mixing time of 10 minutes.

15

The properties of polyester macromolecules are not adversely affected by the grafting reaction. As shown in Table I, the tensile force and the percent elongation of the graft copolymer made from polycaprolactone and maleic anhydride in Example 1 was not impaired when compared to polycaprolactone 787. Table 1 also shows that the tensile strength of a mixture containing only a polyester macromolecule and a natural polymer

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(Experiment 8) is significantly lower than the tensile strength of a composition containing only polycaprolactone, a composition containing a graft copolymer made of polycaprolactone and maleic anhydride, and a composition containing polycaprolactone, a graft copolymer, and gluten. The table also shows that the tensile strength of a blend containing only 5% of a graft copolymer (Example 6) had comparable tensile strength to a blend containing 30% by weight of graft co-polymer (Example 5) or the control

25

containing only polycaprolactone 787. Therefore, increased amounts of natural polymer and un-modified polyester macromolecules can be used to make a biodegradable composition having satisfactory mechanical properties. Because less modified polyester macromolecules (graft copolymers) are required, the cost of production is decreased.

#### Example-9

A laboratory-scale twin-screw extruder (Haake Instruments, Paramus, NJ) with corotating screws was used for melt blending. The barrel length to diameter ratio was 10:1 and the extruder was divided into four zones. The temperature of the first zone was 65°C and those of second and third were maintained at the temperature of reaction 160°C. The capillary die with a diameter of 0.64 cm and a length of 7.6 cm was maintained at constant 90°C for all runs. The screw speed was varied to obtain various residence time. The percentage of MAH grafted and the tensile strength is shown in Table II.

**Table II. Effect of screw speed/residence time on grafting reaction using an extruder.**

<u>Screw speed/min</u>	<u>Residence time(-min)</u>	<u>% of MAH grafted</u>	<u>Tensile Force(MPa)</u>
4	17	1.60	20.5
7	13	1.41	31.4
10	11	1.28	21.6
13	9	0.98	33.6
45	4	0.61	22.4

Table II shows the effect of residence time and screw speed on the grafting reaction. As the residence time is increased, the graft content is also increased. However, the tensile force is decreased as the residence time increases because the product becomes more rigid.

#### Example-10

Injection molding tests were run on the following four compositions:

1. 60 wt-% Gluten/2.5 wt-% Modified PCL/37.5 wt-% PCL-767;
2. 70 wt-% Gluten/2.5 wt-% Modified PCL/27.5 wt-% PCL-767;

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3. 65 wt-% Gluten/5 wt-% Propylene Glycol/1.0 wt% Modified PCL/29 wt-% PCL-787; and
4. 75 wt-% Gluten/2.5 wt-% Modified PCL/22.5 wt-% PCL-767.

The processing conditions for each sample are summarized in Table III. The properties of each sample are summarized in Table IV.

**Table III.**

**Processing conditions for blends in Example 10.**

Sample	EXTRUSION PROCESSING				INJECTION MOLDING		
	Pressure (psi)	Torque (N-m)	RPM	Temp (C)	Ini. temp/ mold temp.	RPM	IP/BP (bars)
#1	1337	26	60	60/110/110/90	100/35	80	120/50
#2	1795	33	60	60/110/110/90	105/35	80	120/50
#3	2422	43	60	60/110/110/90	110/45	80	160/50
#4	1841	37	60	60/110/110/90	110/45	80	145/80

**Table IV.**

**Summary of injection molded gluten/PCL blends in Example 10.**

Sample	Tensile Strength (MPa)	% Elongation	Flex Strength (MPa)
#1	20-22	5-6	36-38
#2	19-21	2.2-6.5	40-42
#3	23.5-25	8-10	36-38
#4	21.5-23	4-6	40-42

The results in Tables III & IV show that a only small amount of graft copolymer, such as polycaprolactone grafted with maleic anhydride, is needed to maintain the tensile properties in a blend containing a natural polymer and a polyester macromolecule. The results in Table IV demonstrate that only a small amount of a graft copolymer (1.0% to 2.5%) is needed to improve the tensile strength of a polyester-natural polymer blend.

**WHAT IS CLAIMED IS:**

1. A graft copolymer comprising a reaction product of a monomer containing a functional group and a polyester macromolecule wherein the monomer is grafted to the polyester macromolecule by an addition reaction or a substitution reaction.
2. The graft copolymer of claim 1 wherein the polyester macromolecule is selected from the group consisting of polycaprolactone, polylactic acid, esters of polyglycols, polyhydroxybutyrate-co-valerate, polyalknates, and mixtures thereof.
3. The graft copolymer of claim 1 wherein the monomer is an anhydride.
4. The graft copolymer of claim 1 wherein the monomer is selected from the group consisting of maleic anhydride, citraconic anhydride, 2,3-Dimethyl maleic anhydride, n-octodacyl succinic anhydride, maleic acid, crotonic acid, itaconic acid, and mixtures thereof.
5. The graft copolymer of claim 1 wherein the functional group is capable of reacting with a hydroxyl or amine.
6. The graft copolymer of claim 18 wherein the functional group is selected from the group consisting of primary amines, secondary amines, tertiary amines, epoxy, hydroxyl, carboxyl, alkyl halides, oxazoline, anhydrides, isocyanate, nitrile, nitro, acyl halides, alkoxy, aldehydes, ketones, thiols, esters, amides, ethers, urethanes, carbodiimide, urea and combinations thereof.
7. The graft copolymer of claim 1 wherein the free radical initiator is an organic peroxide.
8. The graft copolymer of claim 20 wherein the organic peroxide is selected from the group consisting of di t-butyl peroxide, dicumyl peroxide, dibenzoyl peroxide azocompounds, hydroperoxides, and combinations thereof.

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9. A biodegradable composition comprising a continuous phase and a dispersed phase;  
wherein one phase comprises biodegradable material comprising a natural polymer;  
the other phase comprises a graft copolymer comprising a reaction product of a monomer containing a functional group and a polyester macromolecule; and  
at least a few molecules of the graft copolymer and at least a few molecules of the natural polymer are covalently bonded together at the interface between the dispersed phase and the continuous phase.
10. The composition of claim 9 wherein the graft copolymer has at least one functional group that is capable of reacting with a hydroxyl group of the natural polymer.
11. The composition of claim 9 wherein the graft copolymer has at least one group that is capable of reacting with an amine group of the natural polymer.
12. The composition of claim 9 wherein the natural polymer is selected from the group consisting of a carbohydrate, protein, lipid and combinations thereof.
13. A method of making a biodegradable composition comprising the steps of:
- (a) forming a graft copolymer comprising the reaction product of a monomer containing a functional group and a polyester macromolecule wherein the monomer is grafted to the polyester macromolecule by an addition reaction or a substitution reaction; and
  - (b) forming a biodegradable composition by melt blending a natural polymer and the graft copolymer wherein at least a few molecules of the graft copolymer and at least a few molecules of the natural polymer are bonded together at the interface between a dispersed phase and a

continuous phase wherein one phase contains the natural polymer and the other phase contains the graft copolymer.

14. A biodegradable article produced by injection molding, extruding, or compression molding a biodegradable composition comprising a continuous phase and a dispersed phase;

wherein one phase is a biodegradable material comprising a natural polymer;

the other phase is a graft copolymer comprising a reaction product of a monomer containing a functional group and a polyester macromolecule wherein the monomer is grafted to the polyester macromolecule by an addition reaction or a substitution reaction; and

at least a few molecules of the graft copolymer and at least a few molecules of the natural polymer are covalently bonded together at the interface between the dispersed phase and the continuous phase.

# INTERNATIONAL SEARCH REPORT

Intern. Application No

PCT/US 97/09543

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F283/02 C08L51/08 C08L67/02 C08G63/91

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C08L C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 711 791 A (ATOCHM ELF SA) 15 May 1996 see page 2, line 31 - page 4, line 28; claims 1-7	1-8
X	PATENT ABSTRACTS OF JAPAN vol. 095, no. 007, 31 August 1995 & JP 07 090033 A (SHOWA DENKO KK), 4 April 1995, see abstract	1,2,5,6
X	US 3 884 994 A (CRITCHFIELD FRANK E ET AL) 20 May 1975 see column 2, line 55-59; claims 1,6	1,2,4-8
A	EP 0 580 032 A (SOLVAY) 26 January 1994 see the whole document	9-14
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 October 1997

Date of mailing of the international search report

28.10.97

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/09543

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
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Information on patent family members

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